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(21) International Application Number: PCT/EP93/03002 (22) International Filing Date: 25 October 1993 (25.10.93) (30) Priority data: 92402938.2 28 October 1992 (28.10.92) EP (34) <i>Countries for which the regional or international application was filed:</i> FR et al. (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (71) Applicant (for all designated States except CA): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).		(72) Inventors: GUICHARD, Philippe ; GRANDVALLET, Pierre ; BARRE, Guy ; Centre de Recherche, Route de Caen, F-76530 Grand-Couronne (FR). HOEK, Arend ; BOON, Andries, Quirin, Maria ; Badhuisweg 3, NL-1031 CM Amsterdam (NL). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS FOR THE PREPARATION OF LUBRICATING BASE OILS (57) Abstract A process for the preparation of a lubricating base oil comprises contacting a hydrocarbon feed with a catalyst in the presence of hydrogen, which catalyst comprises a hydrogenation component supported on an amorphous silica-alumina carrier having a macroporosity in the range of from 5 % vol. to 40 % vol. The hydrocarbon feed is most preferably a slack wax or a synthetic wax. A preferred catalyst for use in the process comprises a combination of one or more of the metals cobalt, iron and nickel, and one or more of the metals chromium, molybdenum and tungsten on an amorphous silica-alumina carrier having a macroporosity in the range of from 5 % vol. to 50 % vol. This catalyst is especially preferred when hydrocarbon feeds are processed comprising significant amounts of nitrogen- and sulphur-containing compounds.		

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PROCESS FOR THE PREPARATION OF LUBRICATING BASE OILS

The present invention is directed to a process for the preparation of lubricating base oils, in particular by the catalytic conversion of a hydrocarbon feedstock in the presence of hydrogen.

5 Lubricating base oils used, for example, in the formulation of engine lubricants and industrial oils, may be prepared from suitable hydrocarbon feedstocks derived during the refining of crude oil.

10 In the conventional manufacture of lubricating base oils, the residue remaining after the atmospheric distillation of crude oil (often referred to as long residue) is further refined using vacuum distillation techniques. Typical products of the vacuum distillation are waxy distillates, boiling in the range of spindle oil, light machine oil and medium heavy machine oil, and a residue
15 (often referred to as short residue).

 The vacuum distillation is normally operated such that the waxy distillates have viscosities at 100 °C falling in a desired range. Spindle oil waxy distillates typically have a viscosity in cSt (mm/sec) at 100 °C in the range of from 3.5 to 6 cSt. Light
20 machine oil waxy distillates typically have a viscosity in cSt at 100 °C in the range of from 6 to 10 cSt.

 Medium heavy machine oil waxy distillates typically have a viscosity in cSt at 100 °C in the range of from 9.5 to 12 cSt.

25 A typical process for the preparation of lubricating base oils comprises subjecting the spindle oil, light machine oil and medium heavy machine oil waxy distillates waxy distillates to further processing in which undesired aromatic compounds are removed, for example, by solvent extraction using N-methyl-pyrrolidone (NMP), furfural or phenol as the solvent. The resulting fractions may
30 then be subjected to a catalytic treatment in the presence of hydrogen, after which the fractions are subjected to a dewaxing

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operation to yield the final lubricating base oil. The short residue may be subjected to a deasphalting treatment and the resulting hydrocarbon stream (often referred to as bright stock) used as a feed for the aforementioned catalytic treatment.

5 During the catalytic treatment, the hydrocarbon feed is contacted with a suitable catalyst in the presence of hydrogen. Typical reactions occurring during this treatment are hydrogenation reactions, hydrodesulphurisation, hydrodenitrogenation, and some hydrocracking, yielding lower molecular weight hydrocarbons. Most
10 importantly, however, wax molecules in the feed are subjected to hydroisomerisation reactions, leading to lubricating base oils having improved viscometric properties, in particular higher viscosity indexes. An ideal catalyst for use in the catalytic treatment would promote the hydroisomerisation reactions, whilst
15 minimising the hydrocracking reactions, thereby resulting in a lubricating base oil having a desirable viscosity index in a high yield.

Catalysts suitable for use in the catalytic treatment combine a hydrogenation component and an acid component. Suitable
20 catalysts are known in the art. For example, most suitable catalysts for use in this treatment are disclosed in British patent Nos. 1,493,620 (GB 1,493,620) and 1,546,398 (GB 1,546,398). GB 1,493,620 discloses a catalyst comprising nickel and tungsten as hydrogenation components, supported on an alumina carrier. The
25 specification of GB 1,546,398 discloses a catalyst comprising, as a hydrogenation component, nickel and/or cobalt in combination with molybdenum, supported on an alumina carrier. In both GB 1,493,620 and GB 1,546,398 the required acidity for the catalyst is provided by the presence of fluorine.

30 It has now been found that catalysts comprising a hydrogenation component supported on an amorphous silica-alumina carrier are particularly suitable for use in the aforementioned catalytic treatment. The amorphous silica-alumina carrier is acidic by nature. Accordingly, it is not necessary for the performance of
35 the catalyst that a halogen, such as fluorine, is present.

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However, surprisingly, it has been found that, in order to achieve a lubricating base oil having the desired viscosity index in a high yield, the amorphous silica-alumina must have a certain pore size distribution. In particular, it has been found that the amorphous silica-alumina should have a certain macroporosity, that is a substantial portion of the total pore volume of the carrier in pores of high diameter.

The dewaxing operation is typically a solvent dewaxing treatment or a catalytic dewaxing treatment. Both treatments are well-known to those skilled in the art. Solvent dewaxing offers the advantage that next to the dewaxed oil a waxstream is produced, often referred to as slack wax.

The preparation of extra high viscosity index lubricating base oils may be performed by subjecting the wax stream produced during the solvent dewaxing of the hydrocarbon product of the catalytic treatment or any other suitable wax stream, like synthetic waxes, to a (further) catalytic treatment in the presence of hydrogen. Most surprisingly, it has been found that the aforementioned catalysts comprising a hydrogenation component supported on a macroporous amorphous silica-alumina carrier are particularly selective in the preparation of an extra high viscosity index lubricating base oil in such a process.

Accordingly, the present invention provides a process for the preparation of a lubricating base oil, which process comprises contacting a hydrocarbon feed with a catalyst in the presence of hydrogen, which catalyst comprises a hydrogenation component supported on an amorphous silica-alumina carrier having a macroporosity in the range of from 5% vol to 50% vol.

Suitable hydrocarbon materials for use as feed to the process of this invention include any waxy distillate boiling in the range of spindle oils, light machine oils, medium heavy machine oils and deasphalted oils. Another suitable hydrocarbon material for use as feed to the process of this invention is a fraction of a hydrocracker bottoms stream, typically boiling in the range of from 350 to 580 °C. The aforementioned feeds may, if desired, be

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subjected to a solvent extraction treatment, for example extraction with furfural, prior to being used as feed for the process. Slack waxes derived from dewaxing operations are very suitable for use as feeds for the process. In addition, synthetic waxes, such as those prepared by a Fischer-Tropsch synthesis may also be used. The process of the present invention has been found most suitable for use in the preparation of an extra high viscosity index lubricating base oil, that is a base oil having a viscosity index typically greater than 135, from a slack wax feed, a synthetic wax feed, or a feed as disclosed in European patent specification No. 400742, that is, a feedstock derived from a waxy crude oil and containing at least 30% by weight wax and having at least 80% by weight boiling above 300 °C and at most 30% by weight boiling above 540 °C, which feedstock has not been treated to remove a lubricating base oil fraction.

The process is conducted at elevated temperature and pressure. Typical operating temperatures for the process are in the range of from 290 °C to 430 °C, preferably in the range of from 310 °C to 415 °C, more preferably in the range of from 325 °C to 415 °C. Typical hydrogen partial pressures are in the range of from 20 to 200 bar, preferably in the range of from 80 to 160 bar, more preferably in the range of from 90 to 160 bar, in particular in the range of from 100 to 150 bar. The hydrocarbon feed is typically treated at a weight hourly space velocity in the range of from 0.5 to 1.5 kg/l/h, more preferably in the range of from 0.5 to 1.2 kg/l/h.

The feed may be contacted with the catalyst in the presence of pure hydrogen. Alternatively, it may be more convenient to use a hydrogen-containing gas, typically containing greater than 50% vol hydrogen, more preferably greater than 60% vol hydrogen. A suitable hydrogen-containing gas is gas originating from a catalytic reforming plant. Hydrogen-rich gases from other hydro-treating operations may also be used. The hydrogen-to-oil ratio is typically in the range of from 300 to 5000 l/kg, preferably from

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500 to 2500 l/kg, more preferably 500 to 2000 l/kg, the volume of hydrogen being expressed as standard litres at 1 bar and 0 °C.

Catalysts for use in the process of the present invention comprise a hydrogenation component supported on an amorphous silica-alumina carrier. Suitable hydrogenation components are the metals of Groups VIB and VIII of the Periodic Table of the Elements, or sulphides or oxides thereof. Preference is given to catalysts comprising as the hydrogenation component one or more of the metals molybdenum, chromium, tungsten, platinum, palladium, nickel, iron and cobalt, or their oxides and/or sulphides.

For use in processes in which hydrocarbon feeds comprising substantial amounts of nitrogen- and sulphur-containing compounds are used, catalysts comprising combinations of one or more of the metals cobalt, iron and nickel, and one or more of the metals chromium, molybdenum and tungsten are preferred. Especially preferred catalysts for use in treating such feeds comprise, in combination, cobalt and molybdenum, nickel and tungsten and nickel and molybdenum. The catalysts are preferably used in their sulphidic form. Sulphidation of the catalyst may be effected by any of the techniques known in the art. For example, sulphidation may be effected by contacting the catalyst with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butylmercaptan. Alternatively, sulphidation may be carried out by contacting the catalyst with hydrogen and a sulphur-containing hydrocarbon oil, such as sulphur-containing kerosine or gas oil. The sulphur may also be introduced into the hydrocarbon oil by the addition of a suitable sulphur-containing compound, for example dimethyldisulphide or tertiononylpolysulphide. The amounts of metals present in the catalyst may vary between very wide limits.

Typically, the catalyst comprises from 10 to 100 parts by weight of the Group VIB metal, if present, preferably from 25 to 80 parts weight, per 100 parts by weight of carrier. The Group VIII metal is typically present in an amount of from 3 to 100 parts by weight,

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more preferably from 25 to 80 parts by weight, per 100 parts by weight of carrier.

Catalysts for use in the treatment of hydrocarbon feeds which contain low concentrations of nitrogen- and sulphur-containing compounds preferably comprise platinum and/or palladium as the hydrogenation component, with platinum being a particularly suitable metal for inclusion in catalysts for such use. Platinum and palladium are typically present in the catalyst in amounts of from 0.05 to 5.0 parts by weight, preferably from 0.1 to 2.0 parts by weight, more preferably from 0.2 to 1.0 parts by weight, per 100 parts by weight of carrier.

The carrier for the catalyst is amorphous silica-alumina. The term "amorphous" indicates a lack of crystal structure, as defined by X-ray diffraction, in the carrier material, although some short range ordering may be present. Amorphous silica-alumina suitable for use in preparing the catalyst carrier is available commercially. Alternatively, the silica-alumina may be prepared by precipitating an alumina and a silica hydrogel and subsequently drying and calcining the resulting material, as is well known in the art.

The catalyst carrier may comprise any suitable amorphous silica-alumina. The amorphous silica-alumina preferably contains alumina in an amount in the range of from 5 to 75% by weight, more preferably from 10 to 60% by weight. A very suitable amorphous silica-alumina product for use in preparing the catalyst carrier comprises 45% by weight silica and 55% by weight alumina and is commercially available (ex. Criterion Catalyst Company, USA).

For the purposes of this specification, the term "macroporosity" is a reference to the fraction of the total pore volume of the carrier present in pores with a diameter greater than 35 nm. References to the total pore volume are to the pore volume determined using the Standard Test Method for Determining Pore Volume Distribution of Catalysts by Mercury Intrusion Porosimetry, ASTM D 4284-88, at a maximum pressure of 4000 bar, assuming a surface tension for mercury of 484 dyne/cm and a contact angle with

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amorphous silica-alumina of 140°. The total pore volume of the carrier as measured by the above method, is typically in the range of from 0.6 to 1.2 ml/g, preferably in the range of from 0.7 to 1.0 ml/g, more preferably in the range of from 0.8 to 0.95 ml/g.

5 The amorphous silica-alumina carrier of the catalyst used in the process of this invention has a macroporosity in the range of from 5% vol to 50% vol. Preferably, the carrier has a macroporosity of at least 10% vol, more preferably at least 15% vol, even more preferably at least 20% vol. Especially preferred catalysts for
10 use in the process comprise a carrier having a macroporosity of at least 25% vol. In a most preferred embodiment the carrier has a macroporosity in any one of the ranges described hereinbefore, in pores with a diameter greater than 100 nm.

15 Catalysts comprising carriers having a high macroporosity may suffer the disadvantage that the catalyst has a low resistance to damage by crushing. Accordingly, the macroporosity is preferably no greater than 40% vol, more preferably no greater than 38% vol, even more preferably no greater than 35% vol. The side crushing strength of the catalyst is suitably above 75 N/cm, more preferably
20 above 100 N/cm. The bulk crushing strength of the catalyst is suitably above 0.7 MPa, more preferably above 1 MPa.

25 It will be appreciated that a major portion of the total pore volume is occupied by pores having a pore diameter smaller than 35 nm, that is meso- and micropores. Typically, a major portion of those meso- and micropores has a pore diameter in the range of from 3.75 to 10 nm. Preferably, from 45 to 65% vol of the total pore volume is occupied by pores having a pore diameter in the range of from 3.75 to 10 nm.

30 In addition to amorphous silica-alumina, the carrier may also comprise one or more binder materials. Suitable binder materials include inorganic oxides. Both amorphous and crystalline binders may be applied. Examples of binder materials comprise silica, alumina, clays, magnesia, titania, zirconia and mixtures thereof. Silica and alumina are preferred binders, with alumina being
35 especially preferred. The binder, if incorporated in the catalyst,

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is preferably present in an amount of from 5 to 50% by weight, more preferably from 15 to 30% by weight, on the basis of total weight of the carrier. Catalysts comprising a carrier without a binder are preferred for use in the process of this invention.

5 The catalyst for use in the process of the present invention may be prepared by any of the suitable catalyst preparation techniques known in the art.

 The carrier may be prepared from the amorphous silica-alumina starting material by methods known to the person skilled in the
10 art. A preferred method for the preparation of the carrier comprises mulling a mixture of the amorphous silica-alumina and a suitable liquid, extruding the mixture and drying the resulting extrudates.

 The mixture to be extruded should, preferably, have a solids
15 content in the range of from 20 to 60% by weight.

 The liquid for inclusion in the mixture may be any of the suitable liquids known in the art. Examples of suitable liquids include water; alcohols, such as methanol, ethanol and propanol; ketones, such as acetone; aldehydes, such as propanal, and aromatic
20 liquids, such as toluene. A most convenient and preferred liquid is water.

 To obtain strong extrudates, the mixture preferably includes a peptising agent. Suitable peptising agents are acidic compounds, for example inorganic acids such as aqueous solutions of hydrogen
25 fluoride, hydrogen bromide and hydrogen chloride, nitric acid, nitrous acid and perchloric acid. Preferably, the peptising agent is an organic acid, for example a mono- or dicarboxylic acid. Preferred organic acids include acetic acid, propionic acid and butanoic acid. Acetic acid is a most preferred acidic peptising
30 agent. Alternatively, peptising may be effected using a basic peptising agent. Suitable basic peptising agents include organic bases, such as fatty amines, quaternary ammonium compounds, alkyl ethanol amines and ethoxylated alkyl amines. Alternatively, inorganic bases, such as ammonia, may be used. Monoethanol amine
35 and ammonia are particularly suitable basic peptising agents.

The amount of peptising agent included in the mixture should be sufficient to fully peptise the alumina present in the carrier material, and can be readily determined by the pH of the mixture. During mulling, the pH of the mixture should preferably lie in the range of from 1 to 6, more preferably from 4 to 6, when using an acidic peptising agent, and in the range of from 8 to 10, when using a basic peptising agent.

To improve the flow properties of the mixture, it is preferred to include one or more flow improving agents and/or extrusion aids in the mixture prior to extrusion. Suitable additives for inclusion in the mixture include aliphatic mono-carboxylic acids, polyvinyl pyridine, and sulfoxonium, sulphonium, phosphonium and iodonium compounds, alkylated aromatic compounds, acyclic mono-carboxylic acids, fatty acids, sulphonated aromatic compounds, alcohol sulphates, ether alcohol sulphates, sulphated fats and oils, phosphonic acid salts, polyoxyethylene alkylphenols, polyoxyethylene alcohols, polyoxyethylene alkylamines, polyoxyethylene alkylamides, polyacrylamides, polyols and acetylenic glycols. Preferred agents are sold under the trademarks Nalco and Superfloc.

The flow improving agents/extrusion aids are preferably present in the mixture in a total amount in the range of from 1 to 20% by weight, more preferably from 2 to 10% by weight, on the basis of the total weight of the mixture.

In principle, the components of the mixture may be combined in any order, and the mixture mulled. Preferably, the amorphous silica-alumina and the binder, if present, are combined and the mixture mulled. Thereafter, the liquid and, if present, the peptising agent are added and the resulting mixture further mulled. Finally, any flow improving agents/extrusion aids to be included are added and the resulting mixture mulled for a final period of time.

Typically, the mixture is mulled for a period of from 10 to 120 minutes, preferably from 15 to 90 minutes. During the mulling process, energy is put into the mixture by the mulling apparatus. The rate of energy input into the mixture is typically from 0.05 to

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50 Wh/min/kg, preferably from 0.5 to 10 Wh/min/kg. The mulling process may be carried out over a broad range of temperatures, preferably from 15 to 50 °C. As a result of the energy input into the mixture during the mulling process, there will be a rise in the temperature of the mixture during the mulling. The mulling process is conveniently carried out at ambient pressure. Any suitable, commercially available mulling apparatus may be employed.

Once the mulling process has been completed, the resulting mixture is then extruded. Extrusion may be effected using any conventional, commercially available extruder. In particular, a screw-type extruding machine may be used to force the mixture through orifices in a suitable dieplate to yield extrudates of the desired form. The strands formed upon extrusion may be cut to the desired length.

The extrudates may have any, suitable form known in the art, for example cylindrical, hollow cylindrical, multilobed or twisted multilobed. A most suitable shape for the catalyst particles is cylindrical. Typically, the extrudates have a nominal diameter of from 0.5 to 5 mm, preferably from 1 to 3 mm.

After extrusion, the extrudates are dried. Drying may be effected at an elevated temperature, preferably up to 800 °C, more preferably up to 300 °C. The period for drying is typically up to 5 hours, preferably from 30 minutes to 3 hours.

Preferably, the extrudates are calcined after drying. Calcination is effected at an elevated temperature, preferably up to 1000 °C, more preferably from 200 °C to 1000 °C, most preferably from 300 °C to 800 °C. Calcination of the extrudates is typically effected for a period of up to 5 hours, preferably from 30 minutes to 4 hours.

Once the carrier has been prepared, the hydrogenation component may be deposited onto the carrier material. Any of the suitable methods known in the art may be employed, for example ion exchange, competitive ion exchange and impregnation. Also, the hydrogenation component may be comulled with the mixture to be extruded. A most preferred method is impregnation, in which the

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carrier is contacted with a compound of the hydrogenation component in the presence of a liquid.

5 A preferred impregnation technique for use in the process of the present invention is the pore volume impregnation technique, in which the carrier is contacted with a solution of the hydrogenation component, the solution being present in a sufficient volume so as to substantially just fill the pores of the carrier material. A convenient method for effecting impregnation is by spraying the carrier with the requisite quantity of the solution.

10 After impregnation, the resulting catalyst is preferably dried and preferably calcined. The conditions for drying and calcining are as set out hereinbefore.

15 If the catalyst is to comprise more than one hydrogenation component, the carrier may be impregnated with each component in turn, or may be impregnated with all the hydrogenation components simultaneously.

20 In a second aspect, the present invention provides the use of a catalyst comprising a hydrogenation component supported on an amorphous silica-alumina carrier having a macroporosity in the range of from 5% vol to 50% vol in a process for the preparation of a lubricating base oil, which process comprises contacting a hydrocarbon feed with a catalyst in the presence of hydrogen.

25 According to a further aspect of this invention, there is provided a catalyst comprising a hydrogenation component on an amorphous silica-alumina carrier having a macroporosity in the range of from 5% vol to 50% vol. Preferred features for the catalyst per se are as hereinbefore described.

30 The hydrocarbon product of the process of the present invention may be further treated using techniques known in the art to recover the desired lubricating base oil. Thus, the hydrocarbon product may be subjected to redistillation stage. Further processing may include a dewaxing stage, either using solvent or catalytic dewaxing techniques. Further processing steps, such as hydrofinishing may also be applied.

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Solvent dewaxing may be carried out using two solvents, the first to dissolve the oil and maintain the fluidity of the hydrocarbon product at low temperatures (methyl isobutyl ketone and toluene being well known solvents for such use) and the second to
5 act as a precipitating agent at low temperatures (methyl ethyl ketone being well known for such application). Typically, solvent dewaxing proceeds by mixing the hydrocarbon product with the solvents whilst heating, to ensure solution. The resulting mixture is then cooled, typically to a temperature in the range of from
10 -10 °C to -40 °C, and filtered to remove the precipitated wax. The solvents may be recovered from the dewaxed oil and the wax and recirculated.

Catalytic dewaxing is typically carried out by contacting the the hydrocarbon product in the presence of hydrogen with a suitable
15 catalyst. Suitable catalysts comprise crystalline silicates, such as ZSM-5 and related compounds, for example ZSM-8, ZSM-11, ZSM-23 and ZSM-35, and other crystalline silicates like ferrierite, mordenite or composite crystalline silicates described in European patent application publication No. 380180, 178699 and 100115.
20 Alternatively, catalysts may be used having high activity for isomerising waxes. (A catalytic dewaxing process which makes use of such catalysts is sometimes referred to as catalytic iso-dewaxing). Examples of suitable catalysts include zeolite β and silico-alumino-phosphates of structure types 11, 31 and 41, as well as related
25 compounds such as silico-alumino phosphate SM-3. The catalytic (iso-) dewaxing may be carried out at temperatures in the range of from 200 °C to 500 °C, hydrogen pressure of from 5 to 100 bar, a hydrocarbon weight hourly space velocity of from 0.1 to 5.0 kg/l/h and a hydrogen-to-oil ratio of from 100 to 2500 l/kg, the volume of
30 hydrogen being expressed as standard litres at 1 bar and 0 °C.

The lubricating base oil produced by the process of the present invention is most suitable for application in the formulation of lubricating oils for many applications, if desired

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in combination with one or more additives and/or base oil fractions obtained via other processes.

The present invention will be further described with reference to the following illustrative examples.

5 Example 1

A catalyst sample, A, was prepared using the following general procedure:

Amorphous silica-alumina (45% wt silica, 55% wt alumina, ex. Criterion Catalyst Company,) and acetic acid (aqueous solution, 10 sufficient to give 6% wt acetic acid on basis of silica-alumina) were combined. Sufficient water was added to give a loss on ignition at 600 °C of 60% wt and the resulting mixture mulled for a period of 40 minutes. Extrusion aid (Superfloc A 1839, 3% wt on basis of silica-alumina) was added and the resulting mixture mulled 15 for a further 5 minutes. The resulting mixture was extruded using a 1" Bonnot extruder with a 1.6 mm cylindrical dieplate insert. The resulting extrudates were dried and thereafter calcined at a temperature of 565 °C for a period of 3 hours.

Two further samples, B and C, were prepared using the 20 above-described general procedure, but varying the amount of water and acetic acid in the mixture being mulled in order to vary the macroporosity of the eventual extrudates.

Each of the three samples was impregnated with an aqueous solution of nickel nitrate hexahydrate and ammonium metatungstate 25 using the incipient wetness technique. The thus impregnated carriers were then dried at 200 °C for 2 hours and subsequently calcined at 500 °C for 2 hours. The resulting catalysts each comprised 5% wt nickel (6.3% wt NiO) and 23% wt tungsten (30% wt WO₃). Each catalyst sample was subsequently sulphided using a 30 gasoil containing dimethyldisulphide.

Each sample was tested for performance in the preparation of a lubricating base oil using the following general procedure:

The catalyst was loaded into a reactor and retained as a fixed bed. A slack wax, having the characteristics set out in Table 1 35 below, was fed to the reactor at a weight hourly space velocity of

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1.0 kg/l/h. Hydrogen was fed to the reactor at an inlet pressure of 140 bar and at a flowrate of 1500 Nl/h. The reaction temperature in each case was adjusted to achieve a wax conversion of 80% wt. A temperature of 383 °C, 387 °C and 391 °C was required for catalysts A, B and C respectively.

The hydrocarbon product was distilled to remove that fraction of the product having a boiling point below 390 °C and further refined by solvent dewaxing at a temperature of -27 °C. The remaining oil was collected, the yield of oil (expressed as % wt of the feed) for each catalyst tested being given in Table 2 below.

Table 1
Slack wax feedstock

Specific Gravity at 70, °C	0.8102
Nitrogen content (mg/kg)	14
Sulphur content (mg/kg)	380
Viscosity at 100 °C (cst)	6.98
Wax content (390+ °C) (% wt) (solvent dewaxing at -27 °C)	65.2
Initial Boiling Point (°C)	337
% wt recovered at	
370 °C	2.6
390 °C	3.8
470 °C	38.0
510 °C	62.5
>510 °C	37.5

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Table 2Yield of Lubricating Base Oil

Catalyst	Macroporosity ¹ (% vol)	Yield (% wt)
A	1.4	33.0
B	11.9	37.5
C	22.3	42.0

¹ Determined by ASTM method D 4284-83.

% vol. measured in pores > 100 nm

Example 2

A catalyst sample, D, was prepared using the following general procedure:

5 Amorphous silica-alumina (87% wt silica, 13% wt alumina, ex. Grace Davison Catalyst Company) and silica source Ludox AS40 (40% wt silica ex. Du Pont) were combined with monoethanolamine to form a mixture. Separately, hydroxyethylcellulose and water were mixed to form a gel. This gel was added to the mixture to give a dough having a loss on ignition at 600 °C of 60 %wt.

10 Extrusion aid (Nalco 7879) was added and the resulting mixture mulled for 1 hour. The resulting mixture was extruded using a Haake Rheocord to produce cylindrical extrudates of 1.6 mm diameter. The resulting extrudates were dried for 3 hours at 120 °C then calcined for 2 hours at 800 °C.

15 Another sample, E, was prepared using the above-described general procedure, but varying the amount of water in the mixture as indicated in Table 3.

Table 3
Composition of D and E

Carrier	D	E
Silica-alumina (%wt)	36.8	35.4
Ludox AS 40 (%wt)	32.9	31.8
Monoethanolamine (%wt)	4.0	3.9
Nalco 7879 (%wt)	1.1	1.0
Hydroxyethylcellulose (%wt)	3.1	3.0
Water (%wt)	22.1	24.9

Both samples were impregnated with an aqueous solution of chloroplatinic acid using the same incipient wetness technique as in Example 1. The impregnated extrudates were then dried at 150 °C for 2 hours and subsequently calcined at 400 °C for 2 hours.

5 The resulting catalysts each comprised 0.8 %wt platinum. Each catalyst sample was subsequently reduced in flowing hydrogen at 400 °C for 2 hours.

Each sample was tested for performance in the preparation of a lubricating base oil using the following general procedure:

10 The catalyst was loaded into a reactor and retained as a fixed bed. A synthetic wax, having the characteristics set out in Table 4 below, was fed to the reactor at a weight hourly space velocity of 1.0 kg/l/h. Hydrogen was fed to the reactor at an inlet pressure of 30 bars and at a flowrate of 1500 Nl/h. The reactor temperature
15 required to convert 60 %wt of the waxes boiling over 370 °C was 340 °C and 336 °C for catalyst D and E respectively.

20 The hydrocarbon product was distilled to remove that fraction of the product having a boiling point below 370 °C and further refined by solvent dewaxing at a temperature of -20 °C. The remaining oil was collected, the yield of oil for each catalyst tested being given in Table 5 below.

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Table 4Synthetic (Fischer-Tropsch) Wax Feedstock

Specific Gravity at 70 °C	0.7760
Viscosity at 100 °C (cSt)	4.859
Initial Boiling Point (°C)	218
% wt recovered at	
330 °C	10
370 °C	20
400 °C	30
430 °C	40
460 °C	50
490 °C	60
520 °C	70

Table 5Yield of Lubricating Base Oil

(at 60 %wt wax conversion)

Catalyst	Macroporosity (1) (% vol)	Yield (% wt)
D	12.1	43.0
E	20.2	49.5

(1) Determined by ASTM method D 4284-83

% vol. measured in pores > 100 nm.

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C L A I M S

1. A process for the preparation of a lubricating base oil, which process comprises contacting a hydrocarbon feed with a catalyst in the presence of hydrogen, which catalyst comprises a hydrogenation component supported on an amorphous silica-alumina carrier having a
5 macroporosity in the range of from 5% vol to 50% vol.
2. A process according to claim 1, characterised in that the carrier has a macroporosity of at least 10% vol, preferably at least 15% vol, more preferably at least 20% vol, even more preferably at least 25% vol.
- 10 3. A process according to either of claims 1 or 2, characterised in that the carrier has a macroporosity no greater than 40% vol, preferably no greater than 38% vol.
4. A process according to any preceding claim, characterised in that the hydrogenation component is selected from one or more of
15 the metals molybdenum, chromium, tungsten, platinum, nickel, iron and cobalt, or their oxides and/or sulphides, preferably one or more of the metals cobalt, iron and nickel or their oxides and/or sulphides, in combination with one or more of the metals chromium, molybdenum and tungsten, or their oxides and/or their sulphides.
- 20 5. A process according to any preceding claim, characterised in that the amorphous silica-alumina comprises alumina in an amount in the range of from 10 to 75% by weight, preferably from 10 to 60% by weight.
6. A process according to any preceding claim, characterised in
25 that the operating temperature is in the range of from 290 °C to 430 °C, preferably from 310 °C to 415 °C, more preferably from 325 °C to 415 °C.
7. A process according to any preceding claim, characterised in that the hydrogen partial pressure is in the range of from 20 to
30 200 bar, preferably from 80 to 160 bar, more preferably from 90 to 160 bar, even more preferably from 100 to 150 bar.

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8. A process according to any preceding claim, characterised in that the hydrocarbon feed is processed at a weight hourly space velocity in the range of from 0.5 to 1.5 kg/l/h, preferably from 0.5 to 1.2 kg/l/h.
- 5 9. A process according to any preceding claim, characterised in that hydrogen is provided in an amount to give a hydrogen-to-oil ratio in the range of from 300 to 5000 l/kg, preferably from 500 to 2500 l/kg, the volume of hydrogen being expressed as standard litres at 1 bar and 0 °C.
- 10 10. A process according to any preceding claim, characterised in that the hydrocarbon feed is a waxy distillate of a spindle oil, a light machine oil or a medium heavy machine oil, a deasphalted oil, a slack wax or a synthetic wax, preferably a slack wax or a synthetic wax.
- 15 11. A catalyst comprising a hydrogenation component on an amorphous silica-alumina carrier having a macroporosity in the range of from 5% vol to 50% vol.
12. A catalyst according to claim 11, comprising a combination of one or more of the metals cobalt, iron and nickel, and one or more
- 20 of the metals chromium, molybdenum and tungsten on an amorphous silica-alumina carrier having a macroporosity in the range of from 5% vol to 50% vol.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/03002

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C10G45/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,1 568 754 (IFP) 30 May 1969 see claims 1-5 see examples 1-4 ---	1-4,6-12
P,A	EP,A,0 537 969 (TEXACO) 21 April 1993 see claim 1 see page 5, line 12 ---	1-6,8-12
X	US,A,4 705 767 (GRACE) 10 November 1987 see claims 1,7 see column 2, line 53 - line 63 see table 2 ---	11
X	EP,A,0 157 674 (COMPAGNIE FRANCAISE DE RAFFINAGE.) 9 October 1985 see claims 1,5-7 -----	11,12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/03002

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